# Inorganic Carbon Analysis by Modified Pressure-Calimeter Method

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## ABSTRACT

Soil organic C (SOC) analyses using high temperature induction furnace combustion methods have become increasing popular because of advances in instrumentation. Combustion methods, however, also include C from $CaCO_3$ and $CaMg(CO_3)_2$ found in calcareous soils. Separate analysis of the inorganic C (IC) must be done to correct C data from combustion methods. Our objective was to develop a efficient and precise IC method by modification of the pressure-calimeter method. We modified the method by using Wheaton serum bottles (20-mL and 100-mL) sealed with butyl rubber stoppers and aluminum tear-off seals as the reaction vessel and a pressure transducer monitored by a digital voltmeter. Our gravimetric IC determination of six soils showed a strong correlation when regressed against IC from the modified pressure-calimeter method (slope of 0.99, $r^2 = 0.998$). The method detection limit (MDL) was 0.17 g IC $kg^{-1}$ for the 20-mL serum bottles and the limit of quantification (LOQ) was 0.30 g IC $kg^{-1}$. The 100-mL serum bottle had a MDL of 0.42 with a LOQ of 2.4 g IC $kg^{-1}$. When using a 100-mL Wheaton serum bottle as the reaction vessel with a 0.50-g sample size, soils containing up to 120 g IC $kg^{-1}$, which represent a 100 % $CaCO_3$ equivalent, can be analyzed within the V output range of the pressure transducer. Soil organic C determined by subtraction of IC from total C from combustion analysis correlated well with SOC determined by the Walkley-Black.

$\mathbf{S}$OIL CARBONATE analysis methods typically utilize acid dissolution with the consumption of $H^+$ or the determination of Ca and Mg, or $CO_2$ production (Loeppert and Suarez, 1996). Quantitative determination of carbonates can be accomplished using the gravimetric method based on the reaction of HCl with soil carbonates and the gravimetric loss of $CO_2$ as described by the U.S. Salinity Laboratory Staff (1954). This method however is not practical for large sample runs and is not suitable for low IC contents. The measurement of $CO_2$ is preferred because of its simplicity and because it is a direct measure of carbonate when precautions are used to eliminate organic matter oxidation which would give a positive interference (Loeppert and Suarez, 1996). The analysis of $CO_2$ by pressure-calimeter method described by Loeppert and Suarez (1996) is a direct, accurate and inexpensive method, but the complexity of the pressure calimeter apparatus makes large sample runs impractical. The volumetric IC analysis system described by Wagner et al. (1998) improved the pressure-calimeter apparatus by utilizing a pressure transducer, which is monitored by a data acquisition card connected to a personal computer. However, the reaction vessel used by Wagner et al. (1998) is susceptible to leaks, and therefore requires leak checks while the reaction takes place in a constant temperature bath.

Wagner et al. (1998) showed that inorganic C determined as the difference between total C by combustion furnace and SOC where soils are acidified before combustion had a close correlation with their volumetric IC system. However, at concentrations <5.0 g IC $kg^{-1}$, the combustion method difference was less precise. This determination also requires the sample be run twice through a dry combustion system which dramatically increases the cost of the analysis. Acidification of soils prior to analysis by dry combustion is also time-consuming and presents difficulties because destruction of organic matter can occur (Nelson and Sommers, 1996).

We propose a modification of the reaction vessel which facilitates effective analysis of batch runs of 80 to 120 samples per day. Our main objective was to develop a fast and routine method that could produce quantitative analysis of total IC for both extremes of the analytical range. Five subobjectives were (i) to compare gravimetrically-determined IC with IC determined by our modified pressure-calimeter method; (ii) to determine the MDL and the LOQ; (iii) to evaluate the effect of reducing the sample size on precision; (iv) to evaluate the time required to neutralize a range of carbonate-containing soils; (v) to compare the SOC values obtained from combustion analysis corrected with this method to those SOC values obtained from a Walkley–Black analysis.

## MATERIALS AND METHODS

### Apparatus Description

The modified calimeter apparatus (Fig. 1) consists of a pressure transducer (Model 280E Serta, 0-105 kPa, output .03–5.03 VDC from Setra Systems, Inc., Boxborough, MA)[1] connected to a power supply (24 V DC) with 14 gauge wire, and a digital voltmeter wired in line to monitor output from the transducer. Attached to the base of the pressure transducer is 20 cm of clear laboratory Tygon R-3603 tubing (9.5-mm i.d.) connected to an 18 guage Luer-loc hypodermic needle with a particle filter (0.6 μm for removing particles from carrier gas, Leco #768-980; Leco Co., St. Joseph, MI) spliced in the middle of the tubing to prevent any reflux from reaching the pressure transducer (Fig. 1). A 20-mL wheaton serum bottle (Wheaton Science Products, Millville, NJ) serves as the reaction vessel for soils containing up to 18 g IC $kg^{-1}$ and a 100-mL bottle for soils above 18 g IC $kg^{-1}$, in which a 2-mL (0.50 dram) autosampler vial is inserted containing 2-mL of the acid reagent of 6 $M$ HCl containing 3% by weight of $FeCl_2 \cdot 4H_2O$ (Fig. 2). The $FeCl_2$ is used to eliminate the release of $CO_2$ from organic matter (Loeppert and Suarez, 1996). The 2 mL of acid reagent is able to neutralize up to 72 g IC $kg^{-1}$.

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[1] Mention of a commercial product does not impy either USDA–ARS or Colorado State University endorsement of that product or similar products.
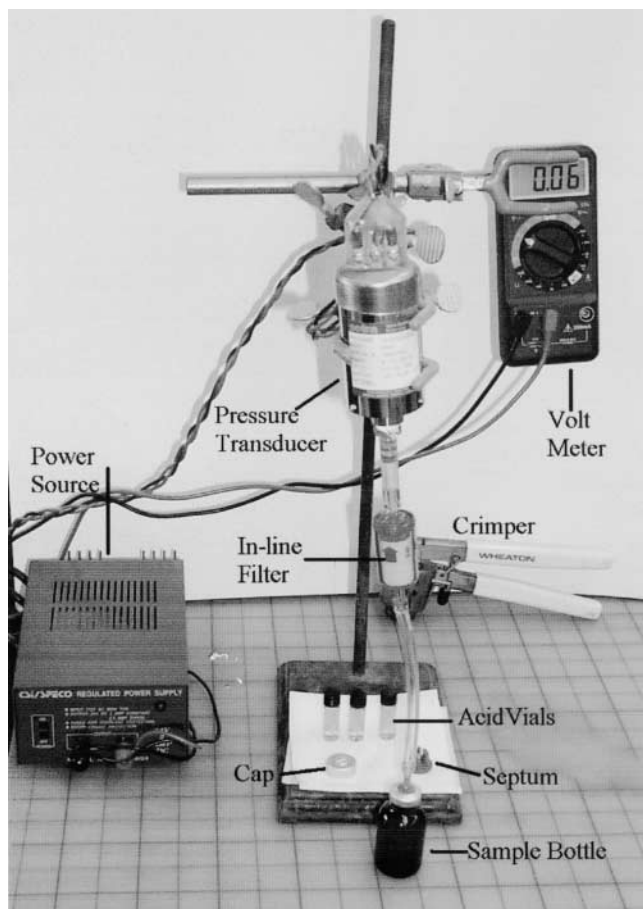
**Fig. 1. Total inorganic C apparatus by modified pressure calcimeter method using Wheaton serum bottles (Wheaton Science Products, Millville, NJ) as the reaction vessel.**

## Analysis Procedure

Soil samples ground to pass through 200-μm (80-mesh) sieve were weighed to 1.00 or 0.50 g and transferred to a Wheaton serum bottle (Wheaton Science Products, Millville, NJ). The vial containing 2-mL of 6 $M$ HCl was then dropped into the serum bottle. The bottle was sealed with a two-prong gray butyl rubber stopper and crimped closed with a aluminum tear-off cap seal using a hand-held crimper. Once the serum bottle with the sample and acid vial was sealed (reaction vessel), the reaction was started by vigorously shaking the 20-mL serum bottle or gently swirling the 100-mL serum bottle assembly to spill the acid vial within the reaction vessel, which allows acid contact with the soil sample. We insured that all of the acid comes in contact with the soil without splashing the soil/acid mixture in the 100-mL reaction vessel up the side walls of the serum bottle. Less care was needed for the 20-mL reaction vessel because of the surface area and rolling the bottle on it's side allowed complete contact of the soil with the acid. After a set reaction time, we measured samples and standards for $CO_2$ evolution by removing the aluminum tear-off seal cap, which exposes the butyl rubber stopper, and inserting the 18-gauge hypodermic needle that was attached to the pressure transducer and voltage meter and recorded the voltage output out to two decimal places after ~3 to 5 s. A calibration curve was developed by mixing reagent grade $CaCO_3$ with oven-dried laboratory sand which was ground to 200 μm (80 mesh). Standards were made based on a final weight of 20.0000 g of sand and $CaCO_3$ to obtain IC concentrations of 0.24, 0.30, 0.60, 1.2, 2.4, 6.0, 12.0, and 18.0 g kg$^{-1}$ for the 20-mL Wheaton serum bottles (Wheaton Science Products, Millville, NJ) (Fig. 3). The calibration curve for the 100-mL Wheaton serum bottle (Wheaton Science Products, Millville, NJ) was obtained using IC concentrations of 0.60, 1.2, 6.0, 12.0, 24.0, 36.0, and 60.0 g kg$^{-1}$ (Fig. 4). A 1.00-g sample of each standard was transfered into the serum bottles. A calibration curve was prepared during each run of samples along with four blanks, the mean of which was used as the zero concentration in the linear regression to account for changes in room temperature and pressure.

## Method Validation

Six soils from the NAPT program were analyzed with four replications using gravimetric determination of total IC with a 1.00-g sample for all soils except 98-119, which was 0.50 g in size (Loeppert and Suarez, 1996). The NAPT program reports median values with median average deviations (MAD) obtained from multiple laboratories (Table 1). The six soils had pH values of 7.8 or greater, and IC values ranging from 2.2 to 37.7 g kg$^{-1}$ as reported in the quarterly results (Table 1). The mean of four replications of our gravimetric IC



**Fig. 2. Wheaton serum bottles (Wheaton Science Products, Millville, NJ) (100 and 20 mL) used as the reaction vessel in the modified pressure calcimeter method for total inorganic C with butyl rubber stoppers and aluminum tear-off sealing caps.**
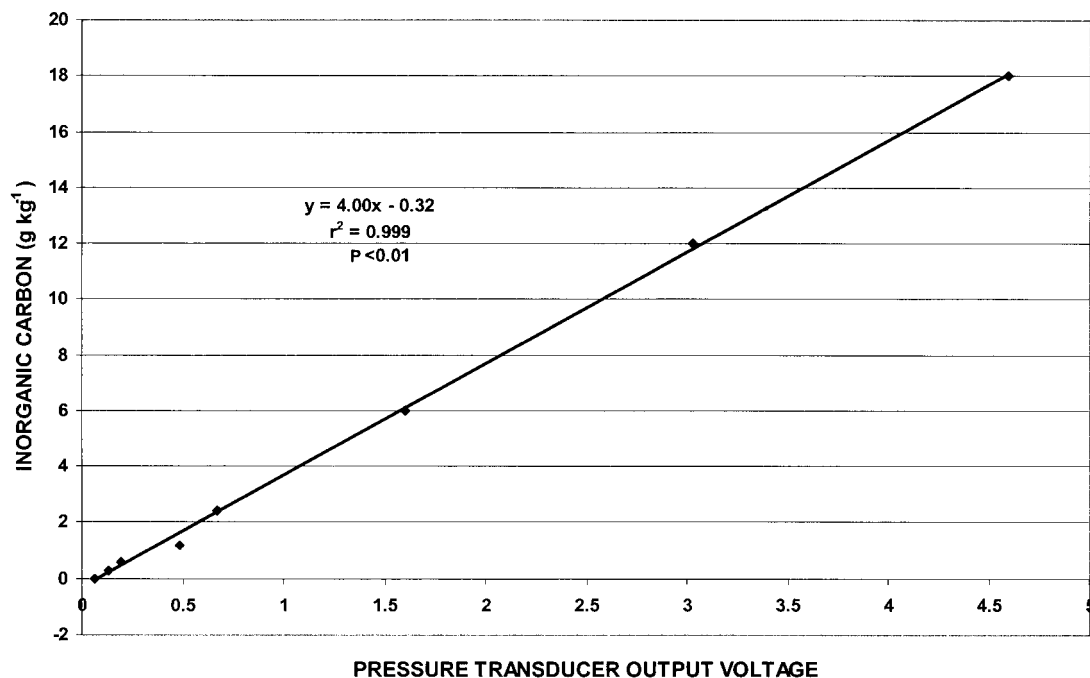
**Fig. 3. Calibration curve for total inorganic C by modified pressure calcimeter using 20-mL Wheaton serum bottles (Wheaton Science Products, Millville, NJ) as the reaction vessel.**

determination for each of the six NAPT soils was compared with our modified pressure-calcimeter method using the mean of four replications for each soil with a 2-h reaction time in a 20-mL serum bottle. The soil sample number 98-119 was weighed to 0.50 g and the remaining five soils were weighed to 1.00-g sample size.

The method detection limit was calculated as three times the standard deviation of 10 method blanks for each reaction vessel (Klesta and Bartz, 1996). In addition to MDL, a limit of quantitation (LOQ) was empirically derived from examining the inflection point in the curve of relative standard deviation (RSD), which is the standard deviation divided by the mean in percentage versus increasing analyte concentration (Klesta and Bartz, 1996). This is defined as the lowest level at which analytical measurement becomes meaningful (Kelsta and Bartz, 1996). Standards were made using reagent grade
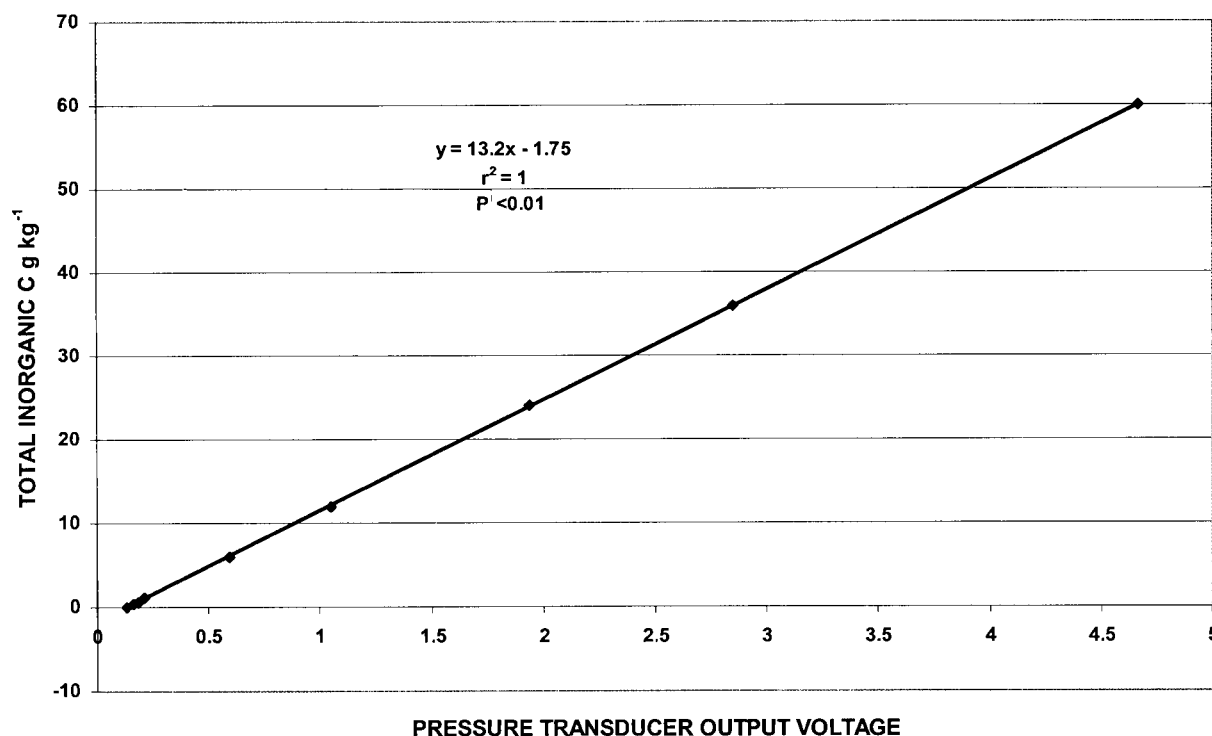


**Fig. 4. Calibration curve for total inorganic C by modified pressure calcimeter using 100-mL Wheaton serum bottles (Wheaton Science Products, Millville, NJ) as the reaction vessel.**

**Table 1. Selected median soil properties as reported by the North American Proficiency Testing program and used in the evaluation of the modified pressure calcimeter total inorganic C analysis.**

| Soil ID | Series | Classification | pH (1:2) | Sand | Silt | Clay | SOC W.B.† | Inorganic C Mean | Inorganic C MAD‡ | Inorganic C RMD§ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | g kg⁻¹ | | | | % |
| 98–105 | Zook | Fine, smectitic, mesic Cumulic Vertic Endoaquolls | 7.8 | 240 | 480 | 280 | 45.2 | 2.2 | 0.7 | 33.3 |
| 99–115 | Sagcove | (Classification not available) | 7.8 | 150 | 480 | 350 | 19.0 | 4.7 | 1.1 | 23.8 |
| 98–114 | Fivemile | Fine-silty, mixed, calcareous, mesic, Typic Torrifluvent | 8.3 | 380 | 410 | 210 | 9.3 | 9.5 | 1.1 | 11.3 |
| 98–104 | Laveen | Coarse-loamy, mixed, superactive, hyperthermic Typic Haplocalcids | 8.4 | 600 | 270 | 130 | 7.5 | 12.6 | 0.7 | 5.4 |
| 2000–103 | Imperial-Glenbar | Fine, smectitic, calcareous, hyperthermic Vertic Torrifluvent | 7.9 | 90 | 380 | 530 | 8.1 | 19.3 | 1.4 | 7.5 |
| 98–119 | Milville | Coarse-silty, carbonatic, mesic, Typic Haploxerolls | 7.9 | 270 | 550 | 180 | 12.4 | 37.7 | 15.0 | 39.8 |

† Walkley-Black soil organic C.
‡ MAD is median average deviation.
§ RMD is relative median deviation.

$CaCO_3$ as described previously in the analysis procedure section with concentrations of 0.12, 0.15, 0.24, 0.30, 0.60, 1.20, and 2.40 g IC kg⁻¹ for the 20-mL reaction vessel. The 100-mL reaction vessel standards were made with concentrations of 0.30, 0.60, 1.20, 2.40, 6.0, 12.0, 24.0, and 36.0 g IC kg⁻¹. Seven replications were weighed out to 1.00 g and transfered into Wheaton serum bottles (Wheaton Science Products, Millville, NJ) for both the 20-mL and 100-mL reaction vessels. These standards and ten method blanks were analyzed using the modified pressure-calcimeter method and the mean, standard deviation, and percentage of relative standard deviation (RSD) were determined for each of the standards. A plot was then produced to show at what concentration the coefficient of variation dramatically increases.

The evaluation of the reduction in sample size from 1.00- to 0.50-g soil mass was done with six replications of each of the six NAPT soils using a 6-h reaction time for both sizes of reaction vessels. The exception to this was sample number 98-119, which could not be run with a 1.00-g sample in the 20-mL reaction vessel because the pressure voltage would have greatly exceeded the transducers 5.03 voltage range.

The effect of reaction time for the six NAPT soils with the acid reagent was evaluated using reaction times of 1, 2, 4, 6, 14, 18, and 24 h. Samples were analyzed using a 1.00-g size and a 20-mL serum bottle as the reaction vessel for soils 98-104, 98-105, 98-114, and 99-115. For soils 98-119 and 2000-103, a 100-mL Wheaton serum bottle (Wheaton Science Products, Millville, NJ) was used as the reaction vessel as their concentrations were above the 18 g IC kg⁻¹ limit imposed by the 20-mL reaction vessel. We analyzed a complete factorial arrangement of seven reaction times and six soils with three replications randomly analyzed within a reaction time. The main factor was reaction time and the subfactor treatment was the soil. We analyzed the data using the GLM procedure of SAS (SAS, 1999).

The six NAPT soils were weighed to 0.2000 g and replicated four times and analyzed for total C by dry combustion using a Leco CHN-1000 (Leco Corp., Saint Joseph, MI; Leco Corp., 1995). The modified pressure calcimeter IC mean from the 6-h reaction time using the 20-mL serum bottle was then subtracted from the total C to obtain SOC for five of the six soils. The IC for sample number 98-119 was obtained by using the 100-mL serum bottle with a 1.00-g sample size. These values were then compared using regression to SOC median values by Walkley–Black (Nelson and Sommers, 1996) reported in the NAPT quarterly results (Table 1).

Surface soils from a long-term dryland no-till cropping system experiment (Peterson et al., 1993) were similarly compared. Surface soil profiles of 0- to 2.5-, 2.5- to 5-, 5- to 10-, and 10- to 20-cm depth increments were sampled in the fall of 1997 at three locations in eastern Colorado at two different cropping intensities (wheat [*Triticum aestivum* L.]-fallow and continuous cropping) and at three landscape positions of summit, side-slope, and toe-slope positions (Peterson et al., 1993). A composite soil sample of 15 to 20 cores using a 2.54-cm i.d. probe was sampled for each slope position within each site location for the each of the rotations. These soils, representing 72 samples, were air dried and ground to passed through a 2-mm sieve, then subsampled before being ground to pass through an 200-μm (80-mesh) sieve. Soils were analyzed for SOC by the Walkley–Black method (Nelson and Sommers, 1996), total C using a CHN-1000 Leco combustion furnace (Leco Corp., Saint Joseph, MI) with a 0.2000-g sample size (Leco Corp., 1995), and IC using our modified pressure-calcimeter method. The total C from the dry combustion was corrected for IC by subtraction to obtain SOC. This value of SOC was then compared by regression to the value of SOC by Walkley–Black analysis.

## RESULTS AND DISCUSSION

Inorganic C median values reported from the NAPT program were in strong agreement with the mean IC values obtained from the modified pressure-calcimeter

**Table 2. Mean soil inorganic C of North American Proficiency Testing program soils as determined by modified pressure-calcimeter (1.00 g sample 2 hr⁻¹) and by gravimetric method.**

| Soil | Modified pressure calcimeter | Standard deviation | RSD§ | Gravimetric | Standard deviation | RSD§ | t value | P > |t| |
|---|---|---|---|---|---|---|---|---|
| | g kg⁻¹ | | % | g kg⁻¹ | | % | | |
| 98–105† | 1.9 | 0.05 | 2.7 | 2.2 | 0.26 | 12.3 | −0.18 | 0.8740 |
| 99–115† | 5.1 | 0.08 | 1.6 | 5.1 | 1.11 | 22.0 | 0.94 | 0.4478 |
| 98–114† | 9.2 | 0.13 | 1.4 | 8.9 | 0.47 | 5.3 | 0.70 | 0.5562 |
| 98–104† | 13.4 | 0.24 | 1.8 | 12.3 | 0.54 | 4.4 | −0.25 | 0.8229 |
| 2000–103‡ | 20.4 | 0.21 | 1.0 | 19.8 | 0.47 | 2.4 | −1.04 | 0.4059 |
| 98–119‡ | 58.3 | 0.65 | 1.1 | 57.8 | 0.58 | 1.0 | −1.39 | 0.2991 |

† 20-mL Wheaton serum bottle used as the reaction vessel with the modified pressure-calcimeter method.
‡ 100-mL Wheaton serum bottle used as the reaction vessel with the modified pressure-calcimeter method.
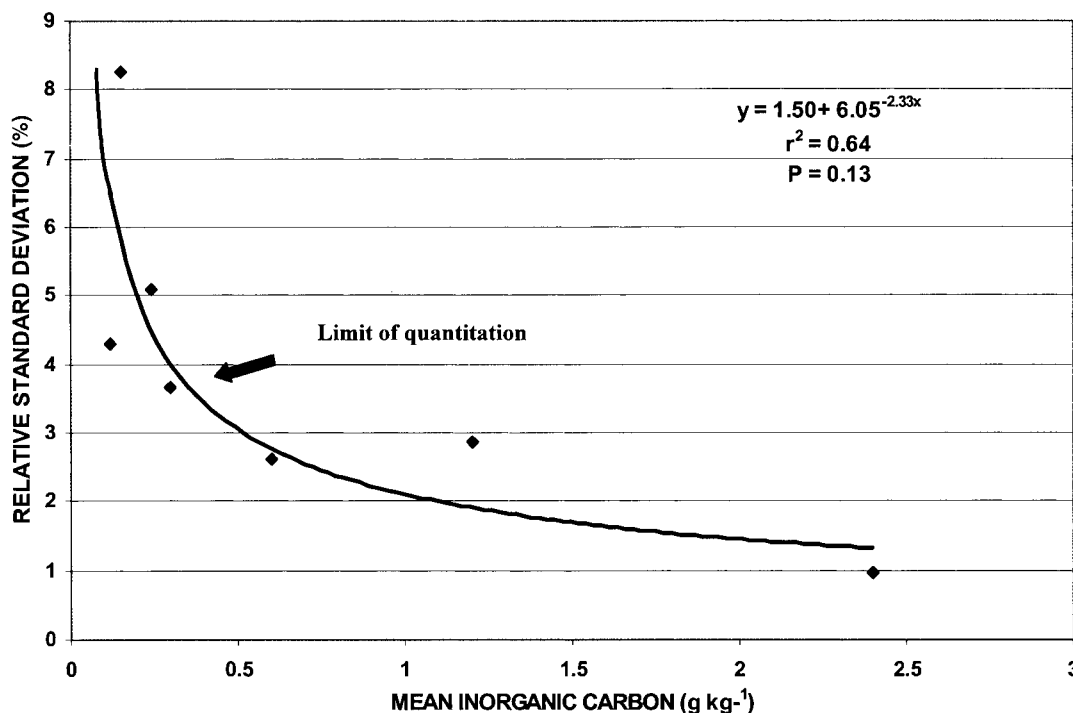§ RSD is relative standard deviation.

Fig. 5.  Limit of quantitation for total inorganic C by modified pressure calcimeter method using 20-mL Wheaton serum bottles (Wheaton Science Products, Millville, NJ) as the reaction vessel.

method for five of the six soils evaluated. The exception soil identified as 98-119 had a reported median value of 37.7 g IC kg$^{-1}$ (Table 1), and a relative median deviation of 39.8%, which is unusually high. In addition, comparison of our gravimetric IC with our modified pressure-calcimeter method IC showed soil 98-119 to contain 57.8 and 58.3 g IC kg$^{-1}$, respectively (Table 2). Statistical comparison for all six NAPT soils showed no significant difference between the IC by gravimetric determination and IC by modified pressure-calcimeter method. A linear regression of gravimetric IC on modified pressure-calcimeter IC for these soils had a slope of 0.991 and an $r^2$ of 0.99.

The method detection limit (MDL) of the modified calcimeter method for the 20-mL Wheaton serum bottle (Wheaton Science Products, Millville, NJ) for IC was 0.17 g kg$^{-1}$. The limit of quantitation (LOQ) for the 20-mL reaction vessel was 0.30 g kg$^{-1}$ (Fig. 5). The 100-mL Wheaton serum bottle (Wheaton Science Products, Millville, NJ) had a MDL of 0.42 and a LOQ of 2.4 g kg$^{-1}$ (Fig. 6). Therefore, soils with $<5.0$ g IC kg$^{-1}$ should be analyzed using a 20-mL serum bottle and soils above 18 g IC kg$^{-1}$ should be analyzed using a 100-mL serum bottle. To determine which reaction vessel to use, soils can be screened by using a 1-h reaction time with a 0.25-g sample size in the 100-mL reaction vessel and the voltages produces by the transducer evaluated. For example, unknowns that produce voltages below 0.50 would need to use the 20-mL reaction vessel to optimize the detection limit. Samples which produce $>0.50$ but $<1.20$ voltages would produce voltages within the 100-mL reaction vessels calibration curve range for a 1.00-g sample. However, samples which produce $>1.20$ V would also use the 100-mL reaction vessel but with a reduced

sample size from 1.00 to 0.50 g to be within the transducers voltage range.

Reduction of sample size from 1.00 to 0.50 g in the 20-mL reaction vessel decreased the RSD percentage slightly, but did not significantly alter mean IC recovery (Table 3). Relative standard deviations were $<5\%$ for both sample sizes, with the exception of soil 98-105 ($\sim$2 g kg$^{-1}$ IC), which had a high RSD (14.2%) associated with the 1.00-g sample size. This degree of variability may be because of high SOC and a clay content of 280 g kg$^{-1}$, which may have affected the acid-to-soil contact with the larger sample size. Soil 98-119 contained sufficiently high IC ($\sim$60 g kg$^{-1}$ IC) as to be out of the voltage range for the 20-mL reaction vessel for both the 0.50- and 1.00-g sample size. With the 100-mL reaction vessel, reduction of sample size from 1.00 to 0.50 g produced a slightly higher mean IC value (Table 3), but again this was not significant at the 0.05 alpha level. With the exception of soil 98-105, RSD's were generally $>5\%$ for both sample sizes. We would, however, recommend a 1.00-g sample when using the 20-mL reaction vessel to maximize the precision for concentrations $<2$ g kg$^{-1}$ IC as this will produce higher pressure transducer output voltage. For the 100-mL reaction vessel, a maximum sample size of 0.50 g is advised for IC concentrations $>60$ g kg$^{-1}$ as samples in this range will produce output voltages above the pressure transducers range limits. In addition, with the reuse of the serum bottles as reaction vessels, these high pressures can weaken the glass and make them susceptible to breaking.

Reaction time was not independent of the soil factor (Table 4). Five of six soils were found to significantly interact with the reaction time. All soils had the lowest mean for the 1-h reaction time. The reaction time which
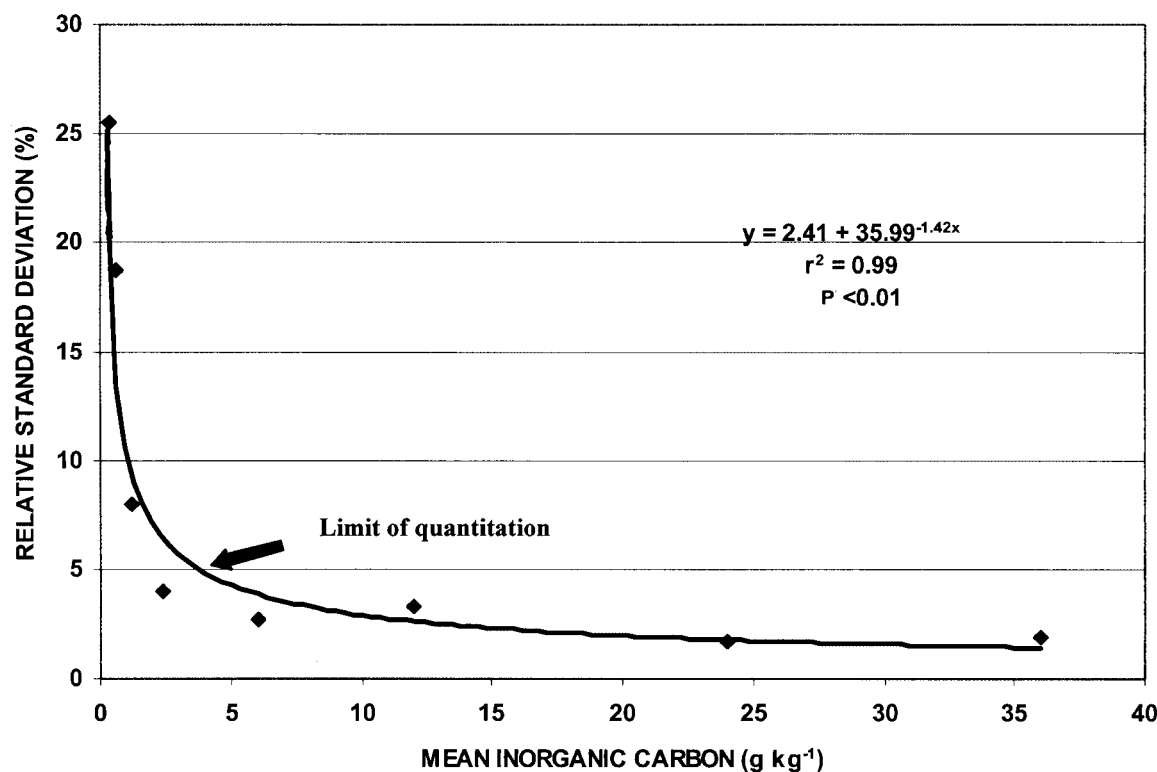
**Fig. 6. Limit of quantitation for total inorganic C by modified pressure calcimeter method using 100-mL Wheaton serum bottles (Wheaton Science Products, Millville, NJ) as the reaction vessel.**

**Table 3. Mean soil inorganic C concentrations of six North American Proficiency Testing soils determined by modified pressure calcimeter as affected by reaction vessel volume and sample size.**

| Soil ID | Mean for 0.50 g | RSD† 0.50 g | Mean for 1.00 g | RSD† 1.00 g | $|t|$ | Pr > t | Mean for 0.50 g | RSD† 0.50 g | Mean for 1.00 g | RSD† 1.00 g | $|t|$ | P > t |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 20 mL reaction vessel | | | | | | 100 mL reaction vessel | | | | | |
| | g kg$^{-1}$ | %g | kg$^{-1}$ | % | | | g kg$^{-1}$ | % | g kg$^{-1}$ | % | | |
| 98–105 | 1.9 | 4.7 | 1.9 | 14.2 | 1.13 | 0.3226 | 1.9 | 14.2 | 1.7 | 4.1 | 1.17 | 0.3086 |
| 99–115 | 5.1 | 1.4 | 5.2 | 5.4 | 0.22 | 0.8383 | 5.2 | 5.4 | 4.9 | 3.7 | 1.16 | 0.3090 |
| 98–114 | 8.9 | 2.8 | 8.9 | 3.6 | 0.10 | 0.9243 | 8.9 | 3.6 | 8.8 | 1.3 | 0.73 | 0.5038 |
| 98–104 | 13.0 | 0.9 | 13.0 | 2.5 | 0.01 | 0.9944 | 13.0 | 2.5 | 12.6 | 2.9 | 2.14 | 0.0994 |
| 2000–103 | 20.3 | 0.6 | 20.0 | 0.7 | 0.75 | 0.4927 | 20.0 | 0.7 | 19.7 | 1.1 | 2.66 | 0.0563 |
| 98–119 | – | – | Out of range | | – | – | 60.0 | 0.5 | 57.0 | 3.5 | 1.33 | 0.2544 |

† RSD is relative standard deviation.

**Table 4. Soil inorganic C by modified pressure calcimeter using a 1.00-g sample in a 20-mL reaction vessel as affected by reaction time with acid.**

| Soil ID | Reaction time (h)† | | | | | | | F Value | P > F | LSD |
|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 4 | 6 | 14 | 18 | 24 | | | |
| | g kg$^{-1}$ | | | | | | | | | |
| 98–105 | 1.70 | 1.80 | 1.76 | 1.90 | 1.70 | 2.23 | 1.96 | 12.57 | <0.0001 | 0.16 |
| 99–115 | 4.83 | 4.96 | 4.93 | 5.13 | 5.00 | 5.30 | 4.83 | 7.71 | 0.0008 | 0.18 |
| 98–114 | 8.60 | 8.83 | 8.96 | 9.20 | 9.03 | 9.23 | 8.77 | 23.98 | <0.0001 | 0.14 |
| 98–104 | 12.46 | 13.0 | 13.13 | 13.36 | 12.90 | 13.03 | 13.0 | 6.42 | 0.0020 | 0.33 |
| 2000–103 | 19.5 | 19.96 | 20.36 | 20.43 | 20.10 | 20.16 | 20.33 | 3.94 | 0.0162 | 0.49 |
| 98–119‡ | 56.3 | 57.40 | 59.10 | 58.07 | 59.33 | 58.83 | 59.20 | 1.73 | 0.1871 | ns§ |

† Reaction time of soil with 6 *M* HCl with 3% FeCl$_2$ reagent.
‡ 100-mL Wheaton serum bottle used as the reaction vessel.
§ Not significant.

released the most IC in a reasonable amount of time was 6 h for most soils. The reaction time did not appear to depend on soil IC concentration, but could be affected by the soil texture.

Soil organic C determined by subtracting total inorganic C by the modified pressure calcimeter from total

soil C by combustion was highly correlated with Walkley–Black SOC for both the NAPT soils and the eastern Colorado soils. The regression of the six NAPT soils had a slope of 1.17 and an $r^2$ of 0.99. The regression of SOC determined by subtracting IC from the total C by combustion against SOC determined by Walkley–Black
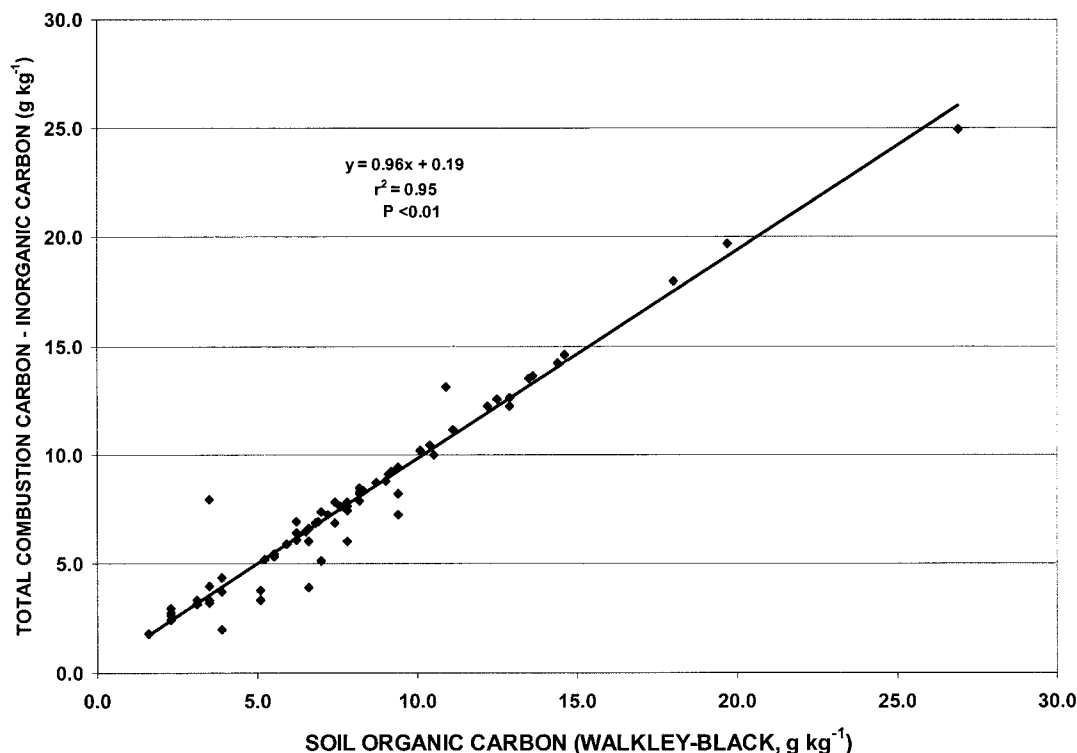
**Fig. 7. Correlation of total soil C by dry combustion minus total inorganic C by modified pressure calcimeter vs. soil organic C by the Walkley–Black method for eastern Colorado soils.**

for 72 eastern Colorado soils had a slope of 0.96 and an $r^2$ of 0.95 (Fig. 7). The Walkley–Black SOC of these soils ranged from 1.5 to 27 g kg$^{-1}$. The IC, using 1.00-g sample size and the 20-mL reaction vessel with a 6-h reaction time, ranged from 0 to 15.7 g kg$^{-1}$. The difference in slopes could be because of the bias associated with varying methodologies across laboratories in the NAPT program. The slopes were not tested for a statistical difference as direct comparisons of the NAPT program results would not be valid because of the potential biases associated with technicians and varying methodologies. These results however, show that the modified pressure-calcimeter method is an accurate way of correcting total C obtained from combustion systems and that it is a reasonable and reliable alternative to the Walkley–Black method for SOC.

## CONCLUSIONS

Our modification of the pressure calcimeter apparatus lends itself to the large sample output needed in commercial and research laboratories. It produces accurate and precise results using simplified techniques and minimal equipment investment. Batch runs of 120 samples per day are possible using a 6-h reaction time and 3 to 5 s per sample for reading output voltage from the pressure transducer after puncturing the reaction vessel rubber stopper. Changes in laboratory temperature and pressure can affect the pressure change in the reaction vessel, and, therefore, a calibration curve is needed for each batch to correct for these changes. By changing the reaction vessel volume size or the sample size, the complete analytical range can be determined with high precision. A reaction time of 6 h is recommended because it resulted in the highest IC value in a relatively short period. Soil organic C determined by total C minus IC was highly correlated with SOC measured by the Walkley–Black method across a wide range of calcareous and noncalcareous soils.

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